



An Innovative System for the Efficient and Effective Treatment of Non-traditional Waters for Reuse in Thermoelectric Power Generation



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ABSTRACT

This study is assessing opportunities for improving water quality associated with coal-fired power generation through the use of innovative technologies focused on recovering and reusing water within power plants. These technologies include specifically designed pilot-scale constructed wetland systems (CWTS) that remove trace inorganic compounds, biocides, and other constituents of concern from non-traditional waters such as cooling waters, flue gas desulfurization waters (FGD), produced waters, and ash basin waters. The objectives of this research include identification of targeted constituents for treatment in the non-traditional waters, determination of reuse or discharge criteria for treatment, design of constructed wetland treatment systems for non-traditional waters, and measurement treatment of targeted constituents. The constituents of concern identified were arsenic (As), chromium (Cr), copper (Cu), mercury (Hg), selenium (Se), and zinc (Zn) in ash basin waters; free oxidants (chlorine, bromine, and peroxides), Cu, lead (Pb), Zn, pH, and total dissolved solids (TSS) in cooling waters; As, boron (B), chlorides (Cl), Se, Hg, chemical oxygen demand (COD), and Zn in FGD waters; and As, cadmium (Cd), Cr, Cu, Pb, Hg, nickel (Ni), sulfide (S²⁻), Zn, TSS, benzene, PAHs, toluene, total organic carbon (TOC), and oil and grease (O&G) in produced waters. Constituents of concern that may cause chemical scaling, biofouling and corrosion, such as pH, hardness and ionic strength, and nutrients [phosphorous (P), potassium (K), and nitrogen (N)] may also occur in all four non-traditional waters.

Based on data collected from FGD experiments, pilot-scale constructed wetland treatment systems can decrease aqueous concentrations of elements of concern (As, Hg, N, and Se). Percent removal was specific for each element, including ranges of 40.1% to 77.6% for As, 77.5% to 97.7% for Hg, 50.4% to 89.8% for N, and no removal to 86.4% for Se. Based on data collected from produced water experiments, hybrid pilot-scale constructed wetland treatment systems can decrease aqueous concentrations of elements of concern (Zn, Cd, Pb, and Cu). Percent removal was specific for each element, including ranges of 38.4% to 99.6% for Cd, 90.6% to 99.8% for Cu, 93.1% to 99.3% for Pb, and 40.0% to 99.8% for Zn from produced waters. Concentrations of As, Se, Cr, and Zn were decreased in ash basin waters by CWTS. Average removal of As, Se, Cr, Zn, and Hg in Ash Basin waters was 88.5, 25.5, 70.4, 68.0, and 94.7%, respectively. Pilot-scale CWTS decrease aqueous concentrations of Cu, Zn, and Pb in cooling waters. Average percent removals for each element in cooling waters were 97.0% for Cu, 30.2% for Pb, and 68.0% for Zn. CWTS were successful in reducing potential for corrosion and biofouling in cooling and ash waters. Pilot-scale CWTS were successful in treating FGD waters, ash basin waters, cooling waters and produced waters.

OBJECTIVES

- 1) Determine the constituents in four non-traditional water
- 2) Determine reuse or discharge criteria for treatment
- 3) Identify the constituents of concern (COC)
- 4) Design pilot-scale constructed wetland treatment systems for COC
- 5) Measure treatment of targeted constituents
- 6) Develop a decision support system for non-traditional waters

EXPERIMENTAL DESIGN

Composition of Non-traditional Waters

- Non- and peer-reviewed articles and chemical analyses of non-traditional water samples

Reuse and Discharge Criteria

- Biofouling, scaling, and corrosion (BSC) potentials, National Pollutant Discharge and Elimination System (NPDES) permits, toxicity values, and irrigation and drinking water standards

Constituents of Concern

- Constituents in non-traditional waters at concentrations exceeding BSC potentials, NPDES permits, and toxicity values.

Pilot-scale CWTS: General Design Principles

- Each system contained two series of a range of reactors
- Hydraulic retention times for each cell (24 to 36 hr)
- Reducing (< -100 mV) and Oxidizing (> -50mV) reactors

Cell 1, 2, and 3:

- 70-150 gallon tubs
- Scirpus californicus*
- Organic matter hydrosol (>5%)

Cell 4 and 5:

- 150 gallon tubs
- Typha latifolia*
- River sand hydrosol

An Example: Pilot-scale CWTS



Sampling and Analysis

- Outflow sampling was conducted at the downstream of each reactor in 1-L high density polyethylene (HDPE) containers
- Inorganic concentrations were analyzed according to standard EPA method 200.7 [Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)]
- Other water chemistry parameters were analyzed using Standard Methods
- Scaling, corrosion, and biofouling were measured using glass and copper coupons and determined as loss or accretion of mass on each coupon

FGD WATER

Constituents of Concern

- Mercury (<0.2 – 58.0 µg/L)
- Zinc (0.13 – 16.2 mg/L)
- Boron (32.5 – 463 mg/L)
- TSS (14 – 1297 mg/L)
- Selenium (0.51 – 17.2 mg/L)
- Arsenic (<0.004 – 4.1 mg/L)
- Chlorides (1496-20163 mg/L)
- COD (32.6 – 3000 mg/L)

Pre-Treated FGD Water

Parameter	Concentrations (mg/L)	Parameter	Concentrations (mg/L)
pH	7.3 ± 0.14	TSS	9.66 ± 8.29
Dissolved Oxygen	8.85 ± 0.73	Hg	0.00171 ± 0.00107
Alkalinity	56.8 ± 3.6	Se	0.0513 ± 0.005
Conductivity	4.19 ± 0.7	As	0.0015 ± 0.0002
Chlorides	1550 ± 140	Nitrogen	12.49 ± 0.92
Sulfate	1718 ± 179		

Percent Removal of Constituents in FGD Water

Sampling Period	% Removal			
	Hg	Se	As	N
1	96.7	NR*	77.6	87.3
2	77.5	NR*	40.1	89.2
3	86.9	NR*	76.4	51.1
4	89.6	14.9	35.9	50.4
5	97.7	28.9	69.2	80.7
6	96.8	35.9	15.0	89.8
7	NM [#]	65.7	66.8	71.4
8	NM [#]	86.4	63.0	81.3

*No removal observed (NR) # Not measured (NM)

*Sampling Period = One hydraulic retention time or 6 days

DISCUSSION / CONCLUSIONS

- Data indicate that constructed wetland treatment systems can decrease aqueous concentrations of As, Hg, N, and Se to meet discharge criteria
- Reuse of treated FGD waters can include discharge to receiving systems, sluicing of bottom ash, and cooling water depending on the ionic strength of these waters

PRODUCED WATER

Constituents of Concern

- Lead (3 - 30 µg/L)
- Zinc (0.017 - 1.6 mg/L)
- Chromium (0 - 0.39 mg/L)
- O&G (non-detect - 78 mg/L)
- PAH (non-detect - 0.11 mg/L)
- Copper (non-detect - 1.24 mg/L)
- Cadmium (0.006 - 0.098 mg/L)
- Chlorides (133 - 108,968 mg/L)

Simulated Produced Waters

Constituent	Chemical Source	Fresh Target Inflow (mg/L)	Brackish Target Inflow (mg/L)	Saline Target Inflow (mg/L)	Hyper-Saline Target Inflow (mg/L)
Chlorides	CaCl ₂ , NaCl	<400-2,500	2,500-15,000	15,000-40,000	>40,000
Cadmium	CdCl ₂	0.4	0.4	0.8	1.2
Copper	CuCl ₂	0.8	1.7	3.3	5.0
Lead	PbCl ₂	1.0	5.5	6.8	10.2
Zinc	ZnCl ₂	5.0	23.0	45.9	69.0
Oil/Grease	Motor Oil	20.0	19.0	49.0	78.0

Pre- and Post-Treated Produced Waters

Simulated Produced Waters	Cadmium (as CdCl ₂) (mg/L)		% removal	Removal Rate (d ⁻¹)
	Inflow	Final Outflow		
Fresh	0.312	0.008	97.6%	0.745
Brackish	0.409	0.252	38.4%	0.121
Saline	1.008	0.004	99.6%	0.705
Hypersaline	1.976	0.008	99.6%	0.686
	Copper (as CuCl ₂) (mg/L)		% removal	Removal Rate (d ⁻¹)
	Inflow	Final Outflow		
Fresh	0.703	Non-Detect	>99.1%	0.953
Brackish	1.052	0.099	90.6%	0.592
Saline	5.314	0.063	98.8%	0.555
Hypersaline	3.498	Non-Detect	>99.8%	0.796
	Lead (as PbCl ₂) (mg/L)		% removal	Removal Rate (d ⁻¹)
	Inflow	Final Outflow		
Fresh	0.744	Non-Detect	>99.1%	0.964
Brackish	2.557	0.176**	93.1%	0.669
Saline	6.012	0.136	97.7%	0.474
Hypersaline	13.170	0.095	99.3%	0.616
	Zinc (as ZnCl ₂) (mg/L)		% removal	Removal Rate (d ⁻¹)
	Inflow	Final Outflow		
Fresh	5.180	0.367	92.9%	0.530
Brackish	21.630	12.985	40.0%	0.128
Saline	48.634	0.374	99.2%	0.608
Hypersaline	79.400	0.185	99.8%	0.758

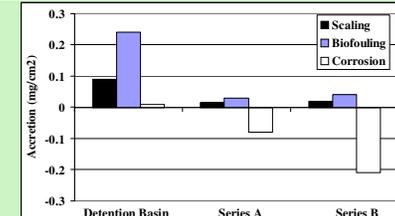
ND indicates a non-detect value was present (ND values were not included in average calculations)
 Detection limit for each element was 0.002 mg Cd/L, 0.006 mg Cu/L, 0.006 mg Pb/L, and 0.005 mg Zn/L
 Removal rate (d⁻¹) is the calculated slope for a first order rate equation: Removal Rate = ln([A]₀/[A]_t)/t

DISCUSSION / CONCLUSIONS

- Data indicate that hybrid constructed wetland treatment systems can decrease aqueous concentrations of constituents of concern in produced waters to meet discharge criteria
- Reuse of treated produced waters can include drinking water, irrigation water, discharge to receiving systems, sluicing of bottom ash, and cooling water

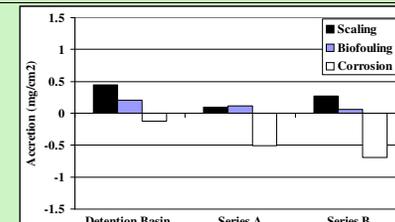
COOLING WATER

Parameter	Copper (mg/L)	Zinc (mg/L)	Lead (mg/L)
Inflow	2.5	1.1	0.139
Outflow	0.075	0.352	0.097
Percent Removal (%)	97.0	68.0	30.2
Removal Rate (d ⁻¹)	0.701	0.227	0.072



ASH BASIN WATER

Parameter	Chromium (mg/L)	Zinc (mg/L)	Mercury (µg/L)	Arsenic (mg/L)	Selenium (mg/L)
Inflow	0.048	0.103	0.015	0.23	0.228
Outflow	0.014	0.033	0.0008	0.026	0.17
Percent Removal (%)	70.4	68.0	94.7	88.5	25.5
Removal Rate (d ⁻¹)	0.246	0.227	0.586	0.435	0.058



DISCUSSION / CONCLUSIONS

- Data indicate that constructed wetland treatment systems can decrease aqueous concentrations of constituents of concern in cooling and ash basin waters to meet discharge criteria
- Reuse of treated cooling and ash basin waters can include drinking water, irrigation water, discharge to receiving systems, sluicing of bottom ash, and cooling water